

CHARACTERIZATION OF LIGNOCELLULOSIC MATERIALS AND MODEL COMPOUNDS BY COMBINED TG/(GC)/FTIR/MS

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INTRODUCTION

Thermal analytical methods have been widely used during the last two decades in the study of biomass thermochemical conversion processes [1-4]. Biomass, which represents a renewable energy resource, consists primarily of plant cells differentiated into characteristic tissues and organs. Lignins, hemicelluloses and cellulose, as the main components of the cell walls, were therefore extensively analyzed, especially from the point of view of their thermochemical reactivity, which is of basic importance for industrial processing of biomass [3].

All types of cellulose microfibrils are composed of linearly linked β -(1 \rightarrow 4)-D-glucopyranose units and differ only by the degree of polymerization. The remaining polysaccharides are known collectively as hemicelluloses and exhibit species related composition. These amorphous, complex heteropolymers characterized by a branched molecular structure exhibit a lower degree of polymerization than cellulose. Xylan is the predominant hemicellulose component of angiosperms ("hardwoods") whereas mannan forms the main hemicellulose of gymnosperms ("softwoods"). The third principal component of biomass, viz. lignin, is an irregular, high MW polymer formed by enzyme-initiated, free-radical polymerization of coniferyl alcohol (in hardwoods), coniferyl plus sinapyl alcohols (in softwoods), or coumaryl alcohol plus both above mentioned alcohols (in grasses) [5]. Lignins act as binding agents for the cellulose and hemicellulose fibers through a variety of linkages involving ether and carbon-carbon bonds of aromatic rings and propyl side chains.

Thermochemical conversion processes of lignocellulosic materials have been studied using mainly thermogravimetry (TG) [6] or flash pyrolysis (Py) followed by gas chromatographic (GC) separation and identification of the reaction products [1]. Modern analytical techniques based on coupled Py-GC/mass spectrometry (Py-GC/MS) [7] or direct Py-MS [2,8] as well as TG/MS or TG/infrared spectroscopy (TG/IR) [4] have proved to be especially useful for elucidating the relationships between biomass structure and pyrolysis/devolatilization mechanisms.

A novel TG/(GC)/FTIR/MS system developed at the University of Utah, Center for Micro Analysis and Reaction Chemistry [9] provides the opportunity for combining accurate weight loss measurements with precise information about composition and evolution rates of gaseous and liquid products as a function of temperature. In this paper, the usefulness of TG/FTIR/MS, TG/GC/MS and TG/GC/FTIR for thermochemical characterization of wood, lignins and cellulose will be discussed.

EXPERIMENTAL

The TG/FTIR/MS system consists of a Perkin Elmer model 7 Thermogravimetric Analyzer with high temperature furnace controlled by an IBM compatible PC and interfaced to a Hewlett-Packard GC/IRD/MSD system (GC - model 5890A, IRD - model 5965A and MSD - model 5971A) controlled by HP 9000 computers (Figure 1). As shown in Figure 1 a specially constructed, heated transfer line assembly allows direct coupling of the TG system to the GC injection port with the GC oven acting as a convenient heated coupling and flow distribution module. In order to make an efficient TG/GC interface, a 0.53 mm I.D. ("megabore") deactivated fused silica capillary column is used to transfer TG effluents to the GC oven. On the TG side this column protrudes several centimeters into a 1 mm i.d. quartz tube which, in turn, extends into the high temperature furnace to within 1 cm of the sample crucible. Both the outlet of the ceramic furnace tube and the quartz tube are vented by means of needle valves. The quartz tube may be also backflushed with helium to prevent air from entering the MSD vacuum system when the TG furnace is open or not yet purged. Inside the GC oven this capillary terminates with a splitter which provides 90 % of the total flow to the IRD and 10% to the MSD instrument. In order to enable GC separations of the TG effluent the capillary transfer line terminates within a specially designed repetitive vapor sampling inlet inside the GC oven. This inlet leads, in turn, to either (or both!) the IRD or MSD modules via a short (ca. 2 m) capillary column. The switching action of the repetitive sampling inlet causes diversion of the "protective" helium gas flow (see Figure 1) allowing only a short (1-2 sec long) burst of TG effluent to enter the column for further GC separation of the various components and subsequent spectroscopic (MS and/or IR) identification.

Samples A steam explosion lignin prepared from Yellow Poplar wood (Liriodendron tulipifera) was isolated by extraction with sodium hydroxide followed by acid precipitation. This sample was donated by Professor Wolfgang Glasser of the Biobased Materials Center at Virginia Tech., in Blacksburg, VA. Douglas fir wood was air dried and analyzed as tiny particles obtained by scratching a piece of wood with a blade.

RESULTS AND DISCUSSION

Figure 2 summarizes some of the results obtained by TG/FTIR/MS analysis of steam explosion Yellow Poplar lignin. In Figures 2b and h the TG weight loss and the differential thermogravimetric (DTG) curves are presented at a heating rate of 15 C/min in helium atmosphere. These graphs reveal the onset of weight loss near 150 C, with a peak of maximum rate of weight loss at 350 C which follows two shoulders at 160 C and 230 C and preceeds a third around 420 C. Averaged mass spectra and infrared spectra of all products evolved during the course of the TG experiment are shown in Figures 2a and g, respectively. Inspection of the MS spectrum indicates the presence of components associated with the monomethoxy series: guaiacol {m/z 124 (M^+) and m/z 109 ($M^+ - 15$)}, 4-methylguaiacol {m/z 138 (M^+) and m/z 123 ($M^+ - 15$)}, 4-vinylguaiacol {m/z 150 and m/z 135}, vanillin {m/z 152} and isoeugenol {m/z 164}. The components associated with the dimethoxy series are syringol {m/z 154 (M^+) and m/z 139 ($M^+ - 15$)}, 4-methylsyringol {m/z 168 and m/z 153}, 4-vinylsyringol {m/z 180}, syringaldehyde {m/z 182} and 4-(1-propenyl)-syringol {m/z 194}. These series of ions are typical for thermal degradation products obtained by pyrolysis of hardwoods or their lignin components [2]. In Figures 2e and f the comparative rates of evolution of guaiacol and syringol are shown as well as 4-methylguaiacol and 4-methylsyringol, respectively. The trace shown in Figure 2k demonstrates the profile of the components exhibiting characteristic alkyl-aryl ether

stretching vibration in the 1260-1290 cm^{-1} region, typical for mono- and di-methoxy phenols, e.g., building blocks of lignin. Our technique enables also the detection of minor contaminants in lignin samples and profiles of the ion m/z 114 (Figure 2d) as well as the trace at 1184 cm^{-1} (Figure 2j), characteristic for C-O stretching vibrations of lactones, strongly suggest the presence such structures as 3-hydroxy-2-penteno-1,5-lactone (M.W. 114) a carbohydrate "marker" from thermal dissociation of xylanes [10] which may be utilized for quantification of hemicellulose residues in lignin preparations. The total ion current (Figure 2b - TIC) and total absorption (Figure 2h - TAP) profiles of the thermal breakdown products released during the TG experiment reveal substantial differences in shape compared to the recorded DTG curve. This is primarily due to the tuning of the MSD instrument for higher masses as well as due to the fact that a high percentage of the weight loss is caused by low molecular weight components (H_2O , CO , CO_2 , MeOH) as demonstrated by the averaged IR spectrum shown in Figure 2g. Nevertheless, the rate of evolution profiles are virtually the same (compare curves in Figures 2c and i for CO_2), hence stronger responses for higher masses facilitate monitoring of high MW components.

Any ambiguities which inevitably arise in regard to the identity of particular components may, to a large extent, be overcome by GC pre-separation of thermal decomposition products. The TG/GC/MS/IR system is capable of separating major products, while still allowing characterization of the evolution profile for particular components, as illustrated in Figures 3 and 4. This enables inspection of selected spectra, providing the way for unequivocal identification and chemical interpretation of thermal processes occurring during the TG experiment. In the TG/GC/MS run of Douglas fir wood vapor samples were taken at 1 minute intervals, so profiles for each GC peak can be followed by identifying peaks with the same GC retention time. This task is greatly facilitated by the selection of characteristic ions at m/z 114, 98, 109 and m/z 138, as shown in Figures 3 b-e. The mass spectrum of the component eluting at 8.31 min is shown in Figure 3f and contrasted with a library spectrum of 3-hydroxy-2-penteno-1,5-lactone (Figure 3j), a typical thermal fragment of the pentose moieties. The mass spectrum of the component taken 11.21 min (Figure 3g) shows spectra of polyhexose pyrolysis products, viz. furanone-2 (M.W. 84) and 5-methylfuranone-2 (M.W. 98) which are the products of depolymerization and further decomposition of cellulose [11]. For the temperature range 350-450 C profiles taken at m/z 109 and m/z 138 can be fully confirmed as representing guaiacol and methylguaiacol fragment and molecular ions, respectively, derived from lignin. This is clearly shown by comparison of the mass spectra taken at 11.53 min and 12.99 min with library spectra (Figure 3).

Results of the TG/GC/IR analysis of Douglas fir wood are reported in Figure 4. In Figure 4 a TG and DTG curves are contrasted with total absorption chromatogram (TAC) profiles recorded at 1 minute intervals each minute after "injection" of the TG vapors, whereas the averaged FTIR spectrum of all volatile components is shown in Figure 4b. This spectrum reflects the complex composition of the pyrolysis products and is dominated by gases with strong absorption coefficients, such as CO_2 , CO and H_2O , thereby complicating individual band assignments and chemical interpretations concerning any additional minor components. In Figure 4c a detailed view of an expanded section of the chromatograms shown in Figure 4a is presented (8-24 mins) and the presence of numerous series of peaks is demonstrated. At 24 s retention time a set of chromatographic peaks exists which reach maximum intensity at 11 min. TG run time (265 C). The spectrum of this component contains a strong absorption band at 1184 cm^{-1} , the selected wavenumber chromatograms of which are shown in Figure 4d, indicating the presence of the C-O stretching vibrations of lactones. In addition to the profiles of these main components, showing the correspondence to the 3-hydroxy-2-penteno-1,5-

lactone from hemicelluloses, there are also two additional sets of peaks at retention time 7 s and maximum rate of evolution at 13 min. (295 °C) as well as at 40 s and maximum evolution rate at 16 min. (340 °C). The last profile clearly exhibits an evolution maximum that is coincident with a profile shown in Figure 4e. The components characterized by retention times approx. 30 s and strong absorption at 1810 cm^{-1} , typical for carbonyl absorption of unsaturated lactones, confirm the presence of 2-furanones generated during the thermal breakdown of cellulose. Finally, the third major stage in the pyrolysis of wood is seen in the occurrence of components reaching peak evolution rates in the 17-18 min run time (355-370 °C) range and decreasing relatively slowly afterwards. Strong absorption bands near 1500 cm^{-1} and just below 1300 cm^{-1} indicate the presence of phenol and aryl-alkyl ethers functionalities, as would be expected from the breakdown products of lignin. An infrared spectrum of such component taken at 42 s after sampling (marked with asterisk in Figure 4f) is shown in Figure 4g and is contrasted with a FTIR reference spectrum of guaiacol, presented in Figure 4h.

Characteristics of this technique combine precise temperature information and accurate weight loss with detailed MS and IR response profiles thereby providing detailed information about the mechanisms and kinetics of thermal degradation processes. Chemical interpretations of the components evolved during heating of lignocellulosic materials under a helium atmosphere are greatly facilitated by inspection of the infrared and mass spectra, if necessary after GC pre-separation.

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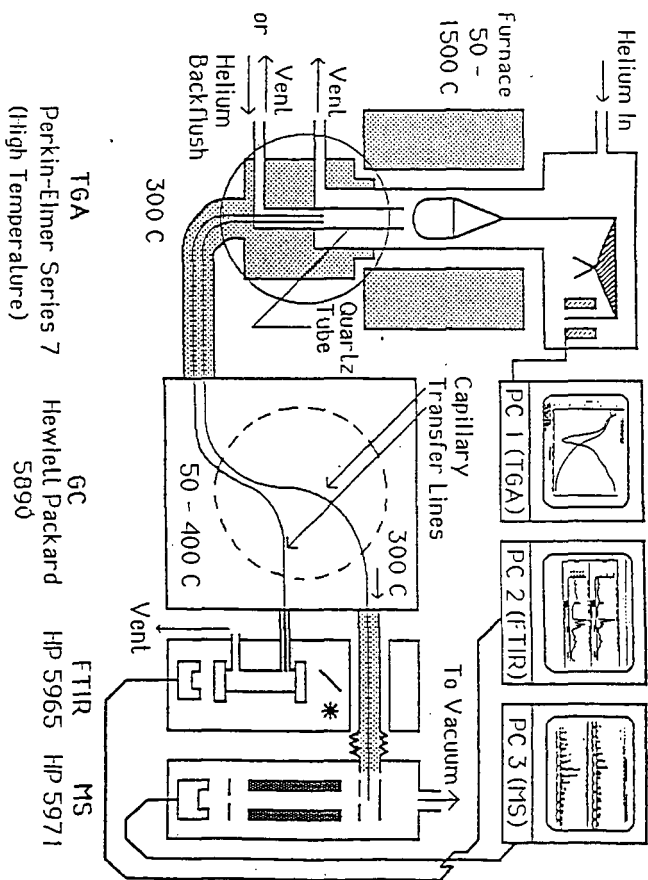


Figure 1. TG/GC/IR/MS instrument configuration.

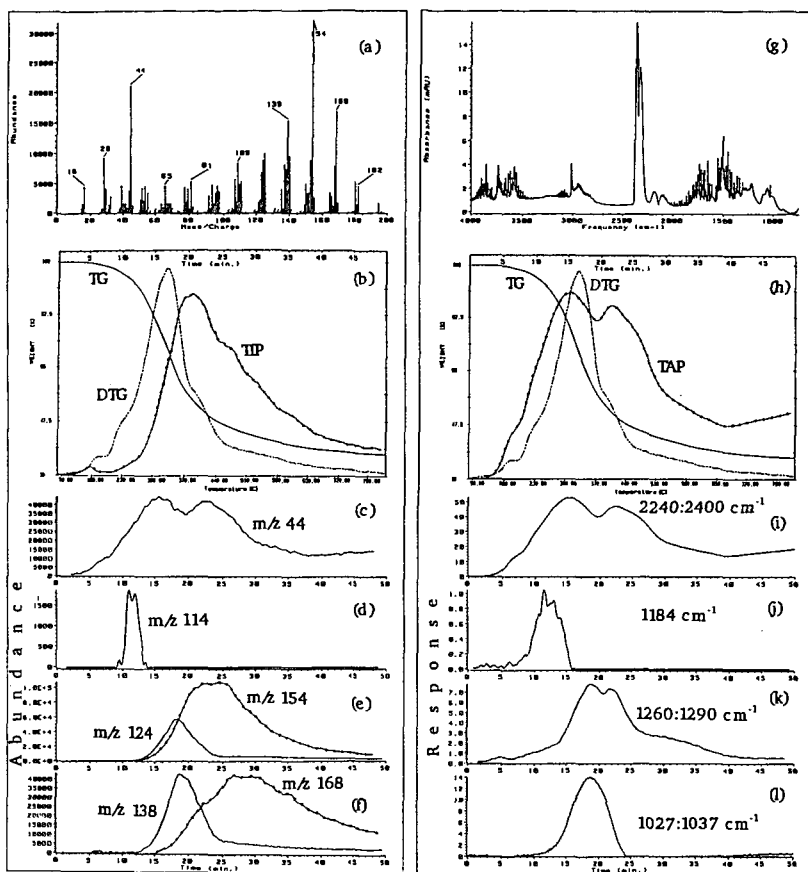
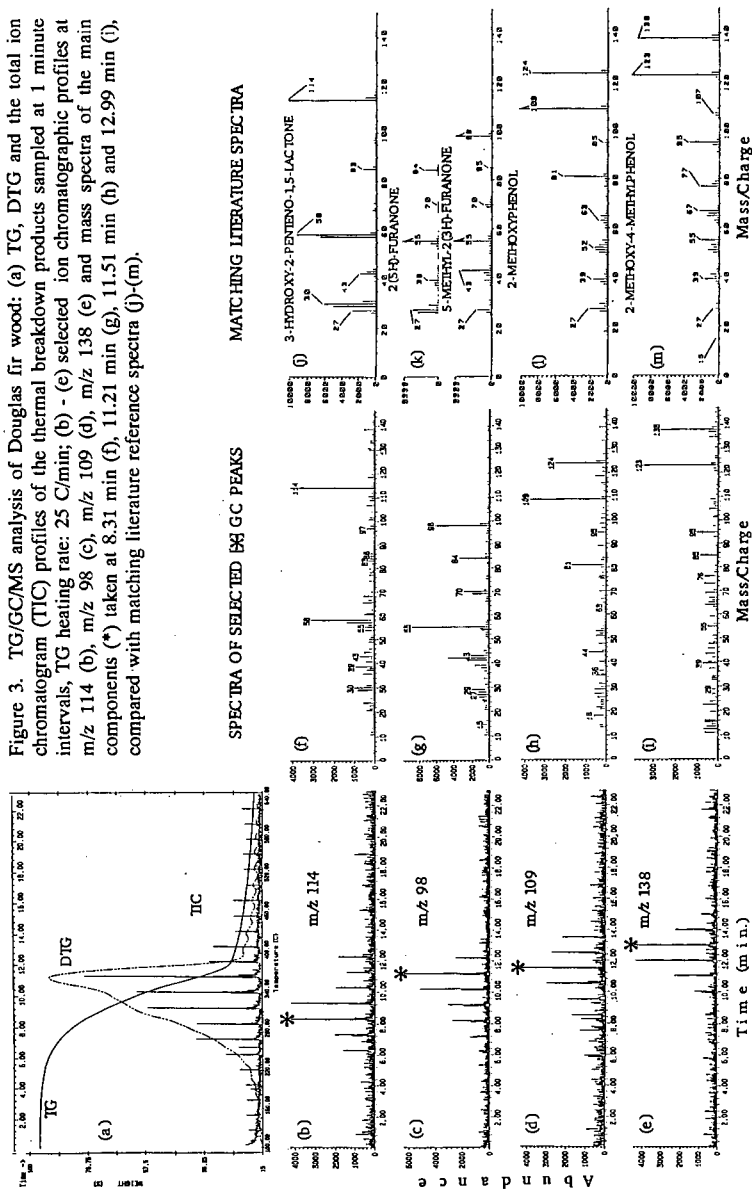


Figure 2. TG/FTIR/MS analysis of steam explosion lignin from Yellow Poplar wood: (a) the averaged MS spectrum of thermal degradation products; (b) TG, DTG and total ion profiles (TIP) of the degradation products; TG heating rate: 15 C/min; (c)-(f) selected ion profiles indicating the evolution of CO_2 (c); 3-hydroxy-2-penteno-1,5-lactone (d); guaiacol (m/z 124) and syringol (m/z 154) (e); 4-methylguaiacol (m/z 138) and 4-methylsyringol (m/z 168) (f); (g) the averaged FTIR spectrum of thermal degradation products; (h) TG, DTG and the total absorption profiles (TAP) of the thermal degradation products; (i)-(l) selected wavenumber profiles indicating the evolution of CO_2 (i), lactones (j), alkyl-aryl ethers (k) and methanol (l).

Figure 3. TG/GCMS analysis of Douglas fir wood: (a) TG, DTG and the total ion chromatogram (TIC) profiles of the thermal breakdown products sampled at 1 minute intervals, TG heating rate: 25 C/min; (b) - (e) selected ion chromatographic profiles at m/z 114 (b), m/z 98 (c), m/z 109 (d), m/z 138 (e) and mass spectra of the main components (*) taken at 8.31 min (f), 11.21 min (g), 11.51 min (h) and 12.99 min (i), compared with matching literature reference spectra (j)-(m).



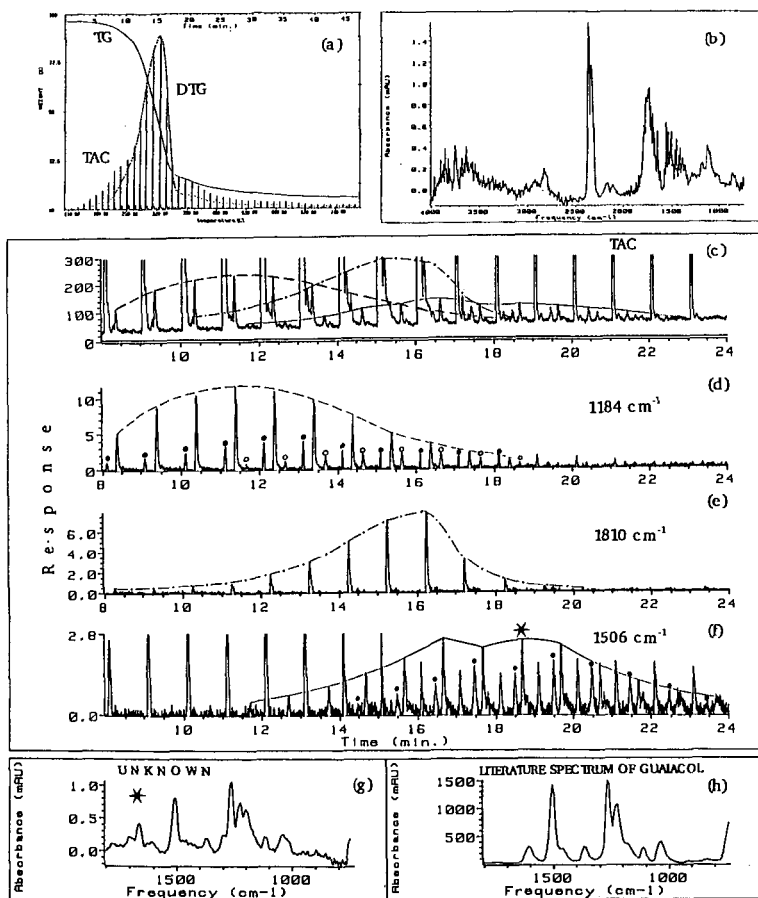


Figure 4. TG/GC/IR analysis of Douglas fir wood: (a) TG, DTG and the total absorption chromatogram (TAC) profiles of the thermal breakdown products sampled at 1 minute intervals, TG heating rate: 15 C/min; (b) the averaged FTIR spectrum of all volatile degradation products; (c) the expanded section of the total absorption chromatogram shown in (a); degradation products from hemicellulose (---), cellulose (---) and lignin (—); (d) - (f) selected wavenumber chromatographic profiles [(d) at 1184 cm⁻¹ (lactones derived from hemicellulose), (e) at 1810 cm⁻¹ (furanones derived from cellulose), (f) at 1506 cm⁻¹ (phenols derived from lignin)]; (g) FTIR spectrum of the unknown component (*) taken at 18.70 min and corresponding to the phenols derived from lignins (---) compared with the reference spectrum of guaiacol (h).